#### STOPPER FOR BOTTLING WINES

# CROSS REFERENCE TO RELATED APPLICATION

[0001] This application is a continuation in part of PCT/IB01/12215 filed November 22, 2001, the teachings of which are incorporated herein by reference.

### BACKGROUND OF INVENTION

[0002] The present invention relates to a stopper to close bottles which is particularly adapted to store and age vintage wines and is made of synthetic material.

[0003] It is well known that wine bottling, more particularly of expensive and consequently valuable wines involves use of glass bottles and corks.

[0004] Corks are specially used to store and age vintage wines because cork allows a limited exchange of oxygen between the bottle interior and the ambient and viceversa. This is the essential condition in order that wine can mature and get refined without deterioration of the wine

[0005] Not all corks can be used to bottle vintage wines and this depends both on quality of cork and the cork production system. Indeed corks made for instance with cork granules joined by an adhesive are not adapted to warrant the correct permeability allowing passage of the required but minimal quantity of oxygen to age and refine wine.

[0006] Another drawback of the corks is the possibility that the cork may keep even after manufacture mould or residues giving a sharp and intense taste to wine, called cork taste.

[0007] Another drawback of the cork consists in that when bottling the cork should have an average moisture not less than 5% and no more than 8%, because a low moisture lower than 5% would cause a too high exchange of oxygen with the ambient while a too high moisture could develop mould.

[0008] If on one hand vintage wines need corks of high quality for their storage and ageing, on the other hand the world production of cork more particularly of high quality, is insufficient to meet the demand of the market of vintage wines.

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[0009] For this reason in the recent times stoppers made of synthetic material were developed, for instance, of polyethylene resins added with a suitable expansion agent, which on one hand can be used to store vintage wines for short periods of time, but on the other hand they are not suitable for their ageing.

[00010] Indeed the stoppers made of synthetic materials allow storage of wine unimpaired relative to the bottling time: wine keeps well its liveliness and freshness without alteration with time, but cannot certainly age because permeability of the synthetic material constituting the stopper reduces the permeability index from 80 to 1000 times in comparison with cork.

[00011] The stopper of synthetic material has however several advantages such as to be mould-proof and bacteria-proof, making the bottled wine exempt from cork taste.

[00012] Another advantage of the synthetic stopper is constancy of quality of said stopper, durability, flexibility and impermeability to liquids.

[00013] One of the limitations of the synthetic stopper is not to allow a correct exchange of oxygen with the ambient in view of its substantial impermeability.

[00014] To this purpose it is to be noted that another limitation of the synthetic stopper consists in that it resists hardly the big temperature difference which a bottle of wine may undergo for instance when left temporarily in the sun, because increase of volume of wine inside the bottle and the substantial impermeability of the synthetic stopper does not allow leakage of an amount of air comprised between the wine level and the bottom portion of the stopper. Consequently phenomena of stopper removal from its seat and movements of the stopper upwards or even ejection from the bottle were observed.

[00015] FR-A-2627467 discloses a flotting cover in a vat of liquid provided with a stopper having a tubular duct having a membrane arranged transversally at the end of said duct. Said membrane allows the passage of the entrapped gasses to escape from the interior of the vat to the outer ambient.

[00016] The object of the invention is to provide a stopper of synthetic material overcoming the above mentioned drawbacks.

## SUMMARY OF THE INVENTION

[00017] A first object of the invention is to provide a stopper of synthetic material having a certain degree of permeability so as to exchange oxygen with the ambient and allow wine contained in the bottle using said stopper to be aged and get refined.

[00018] Another object of the invention is to meter the exchange of oxygen through the stopper with the maximum possible precision so that a certain ageing degree of each kind of wine can be warranted thus reaching the required maximum wine quality. The object is generally to obtain a stopper of synthetic material adapted to meet every requirement according to type of wine and ageing degree.

[00019] The above mentioned objects and others that will be apparent in the following description are attained by a stopper to close bottles, more particularly wine bottles, that according to the main claim is at least partially made of synthetic material and has a generally cylindrical length to be inserted into the bottle neck, said stopper being characterised by having at least a tubular duct adopted to put the residual volume of air inside the bottle in communication with the external ambient through at least a membrane provided with microholes and arranged transversally in said tubular duct allowing the passage of oxygen from the bottle interior to the outer ambient and viceversa.

[00020] It is clear that the present of at least a membrane inside a tubular duct belonging to the stopper, putting the outer ambient in communication with the bottle interior, allows a controlled exchange of oxygen depending on quality of membrane or diameter of its microholes and number of holes per surface unit.

[00021] Advantageously according to the invention the at least one membrane of the stopper is impermeable to liquid passage, while it is permeable to gases and therefore to oxygen in both directions, in other words a two way permeability.

#### BRIEF DESCRIPTION OF THE DRAWINGS

[00022] Further characteristics and features of the invention will be better understood by reading the description of preferred embodiments of the invention given as illustrative but non limiting examples and shown in the accompanying drawing in which:

[00023] FIG. 1 is a perspective and partially sectional view of a stopper of the invention;

[00024] FIG. 1a shows a detail of the membrane of FIG. 1;

[00025] FIG. 1b shows the membrane support tube of the stopper of the invention;

[00026] FIG. 2 is a sectional view of the stopper of FIG. 1;

[00027] FIG. 3 shows another embodiment of the stopper of FIG. 1.

[00028] FIG. 4 shows another embodiment of the stopper of the invention;

[00029] FIG. 5 is a sectional view of a further embodiment of the invention; and

[00030] FIG. 6 is another sectional view of another modification of the invention.

## DESCRIPTION OF THE INVENTION

[00031] With reference now to the drawing one can see that the stopper generally indicated with reference numeral 1 and shown in FIG. 1 and in the sectional view of FIG. 2, is made of synthetic material that in this embodiment is a polyethylene resin added with an expansion agent so as to obtain the characteristics of lightness typical of cork.

[00032] The stopper 1 has a tubular duct indicated with numeral 2 which is arranged in this embodiment along the central axis of the stopper. Approximately at the centre line of said tubular duct there is a membrane 3 of hydrophobic type adapted to allow passage of gases only in both directions. In this embodiment the membrane shown also in FIG. 1a is made of a film of acrylic copolymer 31 anchored to a support that in this embodiment is made of non woven fabric 32. Said support is included in a tube 4 that can be seen also in FIG. 1b, which is inserted in the mould before injection of the acrylic copolymer. It is clear that through the tubular duct 2 extending from the outer surface 21 of the stopper emerging from the bottle to the surface 22

inside the bottle, oxygen may pass proportionally to the size of the microholes of the membrane and the amount of holes involved in the gaseous exchange.

[00033] Therefore it is clear that according to the number of holes and their size, as well as the size of the tubular hole, a controlled exchange of oxygen between inside and outside the bottle can be obtained through the stopper 1. Consequently this allows a controlled and homogeneous ageing degree of wine contained in the bottle. Consequently all the bottles of the same lot of wine can have the same exchange of oxygen and therefore the same maturation.

[00034] Effected tests showed that the exchange of oxygen between bottle and ambient should be about 0.1 mg of oxygen per year to obtain a good wine ageing.

[00035] Consequently according to the type of wine to be treated and results to be obtained, a particular type of membrane or one or more membranes of equal or different type may be chosen.

[00036] Good results were obtained with membranes having diameters or holes varying from 0.01 to 0.5 microns according to the kind of wine treated.

[00037] More particularly, test were carried out with three types of membranes manufactured by the Italian company GVS SpA.

[00038] Each membrane was inserted into a polyester tube and fixed approximately at its center in the horizontal transverse direction as shown in FIG. 2.

[00039] Three types of membranes manufactured by the company GVS were tested.

[00040] All the membranes were of the hydrophobic kind, i.e. liquid repellant, but adapted to let air and therefore oxygen as well pass in both directions.

[00041] The membrane characteristics were the following:

	1	2	3
Membrane	GVS UF 10	GVS UF 100	GVS RO 21
Туре	Hydrophobic	Hydrophobic	Hydrophilic
Configuration	Flat and supported	Flat and supported	Flat and supported
Supporting material	Polyester	Polyester	Polyester
Membrane material	Fluorinated polymer	Fluorinated polymer	Polyamide
Nominal pore size	< 0,01 micron	< 0,01 micron	Dense membrane
	Cut-off = 10 kDlton <sup>1</sup>	Cut-off = 100 kDlton1	NaCl rejection > 99%2
Thickness	100 – 150 micron	100 – 150 micron	100 – 150 micron

[00042] Said tests were carried out by the University of Udine, Italy on membranes of the above mentioned type, consisting of a circular disc with a 5 mm diameter.

[00043] It was found that time required to obtain an exchange of 2 mg oxygen was as follows:

1	2	3
GVS UF 10	GVS UF 100	GVS RO 21
7 days	15 days	34 days

[00044] Obviously with smaller membrane diameters, the amount of oxygen decreases considerably.

[00045] It is deemed that an ideal membrane diameter, and consequently of the hole 2 made in the stretch 1 of FIG. 1, may be of about 1-1.2 mm.

[00046] With such a hole and the membranes used for said tests, good and sufficient levels of exchange of oxygen between bottle interior and outside ambient were obtained, said levels being comparable with those of a cork of the best quality. It was noted that a membrane type GVS RO21 may be suitable to keep and age white wines, while a membrane type GVS UF 100 may be suitable to keep and age red wines.

[00047] In FIG. 3 a first modified version of the invention is shown in which there are two tubular ducts and one membrane for each duct. Indeed the tubular duct 5 has the membrane 6 and the tubular duct 7 has inside the membrane 8.

[00048] The stopper of FIG. 3 the membrane conditions relative to the stopper of FIG. 1 and 2 being equal, allows a double exchange of oxygen between bottle inside and ambient.

[00049] In FIG. 4 another modified version of the invention is shown in which one can see one membrane only indicated with numeral 30 exchanging oxygen between ambient and bottle through two ducts indicated with numerals 9 and 10. Clearly the portion of the membrane that does not match the tubular ducts is generally inoperative.

[00050] FIG. 5 shows another modified version of the invention in which there is only one tubular duct 11 where inside said duct there are two membranes indicated with numerals 13 and 14 and arranged inside the same tube 15.

[00051] Another modified version of the invention is shown in the cross sectional view of the stopper of FIG. 6. In this case the stopper has two tubular ducts 16 and 17 inside each of them two membranes 18 and 19 being arranged for the duct 16 and two membranes 23 and 24 for the duct 17.

[00052] It is known that exchange of oxygen between bottle inside and outer ambient and viceversa occurs particularly with change of temperature of wine which consequently undergoes a volume change. When volume inside the wine bottle increases, there is ejection of oxygen contained inside the bottle, while when wine volume tends to return to the starting volume in view of a temperature reduction, there is introduction of oxygen from outside.

[00053] These movements and exchanges of oxygen as it is well known in the wine field, cause refinement and improvement of wine as well as its preservation that varies from one kind of wine to the other.

[00054] From the foregoing one can see that the invention attains the object to provide a stopper that being made of synthetic material thus having all the advantages of a stopper of synthetic material, at the same time allows also a controlled exchange of oxygen, thus allowing to use said stoppers for bottling vintage wine.